

Anodized alumina films studied by soft x-ray emission spectroscopy

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Al₂O₃ has been an important material for its technical applications, e.g., as a matrix for small metallic particles in the solar absorbers. With appropriate concentration of metallic particles and the appropriate film thickness, anodized Al₂O₃ can be used as good solar absorber with selective properties (1-4). The purpose to create such a structure is to minimise the thermal emittance from the solar absorber.

The samples were prepared in the process of anodization. A 0.5 mm thick rolled electroplated aluminium sheet anodized in diluted phosphoric acid (H₂PO₄) solution at room temperature using a dc voltage of 15 V. These conditions produce a porous amorphous aluminium oxide film with a pore fraction as large as 30 to 40 percent by volume (10,11). The pores are columnar and extend through the oxide layer from the metal-oxide interface to the surface. A very thin barrier layer buffers the Al substrate. The time of anodization was set to around 12 minutes to produce a film thickness of about 500 nm. The oxide thickness was measured using an alpha step 200 mechanical stylus profilometer. The anodizing bath was continuously stirred to minimise local heating of the substrate, which would result in uneven oxide coatings.

The porous aluminium oxide coatings are then filled with metal particles from aqueous salt solution. Three different types of coatings: nickel, copper and copper-nickel pigmented aluminium oxide have been prepared from salt solutions of nickel sulphate (NiSO₄), copper sulphate (CuSO₄) and an equal amount of mixture of NiSO₄ and CuSO₄, respectively. An appropriate ac voltage was applied to the electrodes and the small metal particles were formed as rods with average diameter of 30 nm. The particles started to grow from the pore base (12,13) that possess a volume fraction of about 30 percent (14). Different pigmentation time was used during the sample process and hence different pigmented layer thickness has been produced.

Soft-x-ray emission spectroscopy (SXES) experiment was performed at beamline 7.0.1. (15). The x-ray emission spectra for non-porous Al_2O_3 , porous Al_2O_3 , and porous Al_2O_3 pigmented with Ni were recorded with the grazing incidence soft x-ray fluorescence spectrometer (16-17). The resolution of monochromator and spectrometer is 0.60 eV and 0.22 eV, respectively.

The two emission bands of Al_2O_3 in Figure 2 are primarily derived from Al s-states. The width of the filled band of Al in Al_2O_3 was found 8.5 ± 0.5 eV which is close to previously found value 8.7 eV of Al $\text{L}\alpha, \beta$ emission band spectra of non-porous Al_2O_3 for different excitation 0.2 eV. There are small emission bands, which appear in the region of about 71.2 to 74.5 eV at the excitation energies close to threshold, are shifting with the excitation energies. They are originated from the low-energy excitations in the resonant inelastic x-ray scattering.

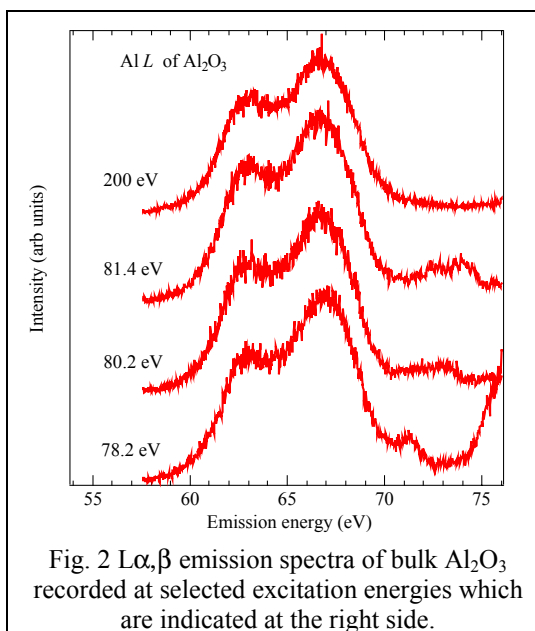


Fig. 2 $\text{Al L}\alpha, \beta$ emission spectra of bulk Al_2O_3 recorded at selected excitation energies which are indicated at the right side.

Fig. 3 shows a series of spectra of porous Al_2O_3 film recorded at different excitation energies. The two characteristic emission bands of Al_2O_3 are still present in the spectra. In addition a sharp cut-off edge can be observed at about 72 eV in all spectra, and its intensity varies some depending on the excitation energy.

The sharp edge at 72 eV indicates the metallic character. Thus, the metallic and oxidized Al are superimposing to each other. It reveals that different Al oxidation levels were created during the anodization process. In the present study photon excitation was used and this 72-eV-edge appears all the time from the excitation energies at threshold up to higher energies, therefore the thermal effects may be neglected. On the other hand, the experimental observation can be explained as the effect of porosity of the material. And the process of anodization may change the oxidation level of the material.

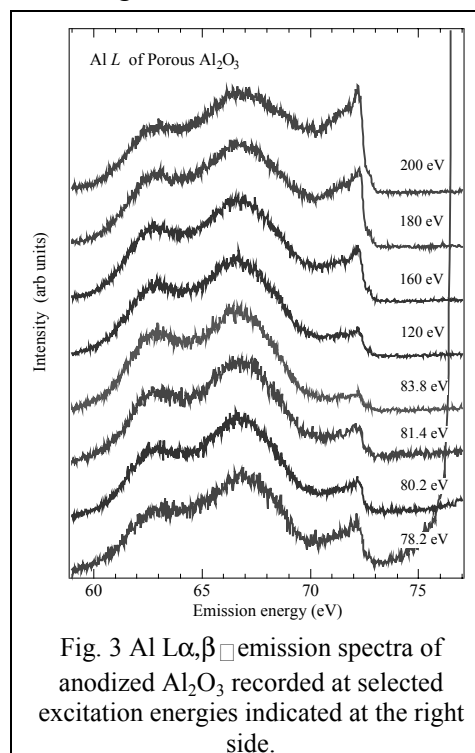


Fig. 3 Al $\text{L}\alpha, \beta$ emission spectra of anodized Al_2O_3 recorded at selected excitation energies indicated at the right side.

The penetration depth of soft x-rays was calculated (not shown) using formulas by

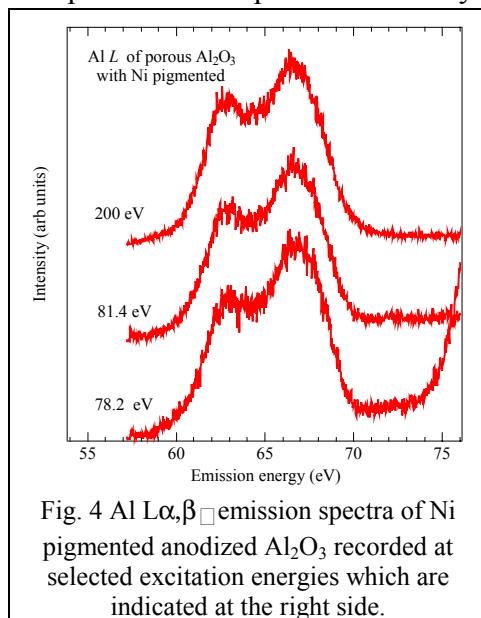


Fig. 4 Al $L\alpha, \beta$ emission spectra of Ni pigmented anodized Al_2O_3 recorded at selected excitation energies which are indicated at the right side.

Henke et al. X-rays with photon energy of 80 - 200 eV can penetrate maximum depth of 200 nm under the present experimental geometry (incident angle of 30°). The porous Al_2O_3 film has a thickness of 500 nm, so the chance for photon-excited-SXES to probe the substrate is removed.

Interesting situation arises when the pores of porous Al_2O_3 have been filled completely with nickel (see in Fig.4). The SXES spectra exhibit again the two-emission-band structure. Metallic Al character has been suppressed after pigmentation. Also, an angular resolved measurement has been performed at different take off angles to check if this metallic peak is still there in case of porous Al_2O_3 . It was

found that metallic Al peak at 72 eV still could be seen in the angular resolved SXES measurements.

We have investigated the electronic structure anodized Al_2O_3 by soft x-ray emission spectroscopy. The Al $L\alpha, \beta$ soft x-ray emission spectra of Al_2O_3 films, in the forms of porous and non-porous, are recorded. Comparison of porous and non-porous Al_2O_3 films has shown that a certain amount of metallic Al is preserved in the porous Al_2O_3 film. Further treatment of the porous film in Ni-pigmented process oxidizes completely the remaining metallic Al in the porous Al_2O_3 film from anodization process.

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This work was supported by the Swedish Science Research Council (VR), the Göran Gustafsson Foundation for Research in Natural Science and Medicine (GGS), and Department of Energy Materials Sciences Division Contract DE-AC03-76SF00098.

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